

Lecture on First-principles Computations (10): Pseudopotential Plane-Wave Method

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Solving the Kohn-Sham equation iteratively

i : iteration step

ϵ : convergence threshold

$0 < \alpha < 1$: mixing parameter

$$n^{(1)}(\mathbf{r}) = n_{trial}(\mathbf{r})$$

$$V_{eff}^{(i)}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int d^3 r' \frac{n^{(i)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[n^{(i)}](\mathbf{r})$$

$$\left(-\frac{\nabla^2}{2m} + V_{eff}^{(i)}(\mathbf{r}) \right) \psi_l^{(i)}(\mathbf{r}) = \epsilon_l \psi_l^{(i)}(\mathbf{r})$$

$$n_{out}^{(i)}(\mathbf{r}) = \sum_{l=1}^N |\psi_l^{(i)}(\mathbf{r})|^2$$

$$\int |n_{out}^{(i)}(\mathbf{r}) - n^{(i)}(\mathbf{r})| dr < \epsilon?$$

no

$$n^{(i+1)} = \alpha n_{out}^{(i)} + (1 - \alpha) n^{(i)}$$

yes

exit

Simple linear mixing here;
More sophisticated mixing
scheme exists.

Single-particle Schrödinger equation in a periodic potential

The key is to solve the single-particle Schrödinger equation:

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$

Consider a periodic potential: $V_{eff}(\mathbf{r}) = V_{eff}(\mathbf{r} + \mathbf{R})$

The eigenstates are Bloch orbitals

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_{l\mathbf{k}}(\mathbf{r}) = \epsilon_{l\mathbf{k}} \psi_{l\mathbf{k}}(\mathbf{r})$$

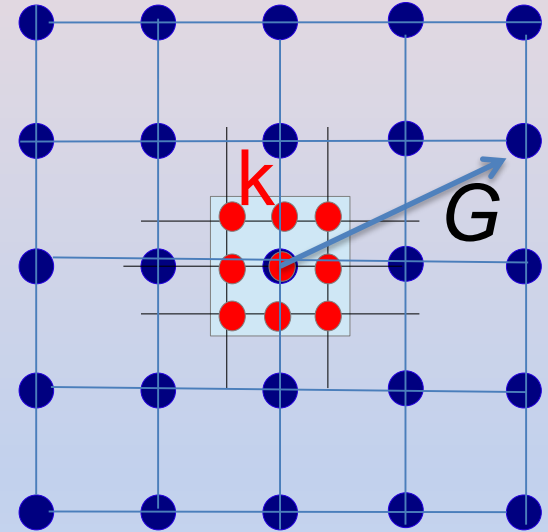
$$\psi_{l\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{l\mathbf{k}}(\mathbf{r})$$

Plane waves as basis functions

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_{l\mathbf{k}}(\mathbf{r}) = \epsilon_{l\mathbf{k}} \psi_{l\mathbf{k}}(\mathbf{r})$$

Plane waves: $|\mathbf{p}\rangle = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{p}\cdot\mathbf{r}}, \langle \mathbf{p} | \mathbf{p}' \rangle = \delta_{\mathbf{p}\mathbf{p}'}$

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$



$$\mathbf{p} = \mathbf{k} + \mathbf{G}$$

Using plane waves to expand the wave function $\psi_{l\mathbf{k}}(\mathbf{r})$:

$$\psi_{l\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{l,\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad V_{eff}(\mathbf{r}) = \sum_{\mathbf{G}} V_{eff}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

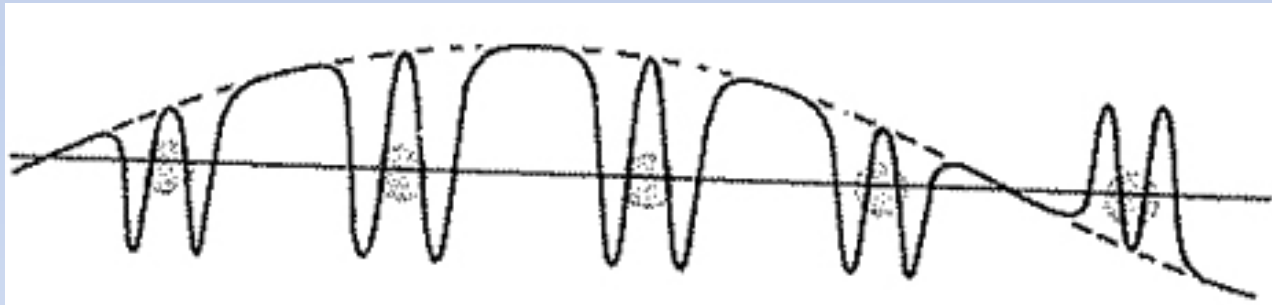
The Hamiltonian matrix:

$$\langle \mathbf{k} + \mathbf{G} | -\frac{\nabla^2}{2m} + V_{eff} | \mathbf{k} + \mathbf{G}' \rangle = \frac{(\mathbf{k} + \mathbf{G})^2}{2m} \delta_{\mathbf{G}\mathbf{G}'} + V_{eff}(\mathbf{G} - \mathbf{G}')$$

Problem: the wave functions oscillates strongly around the nuclei

Observation:

Due to the presence of core electrons, **the valence electron wave function oscillates strongly near the nuclei** (and orthogonalized to the core states).



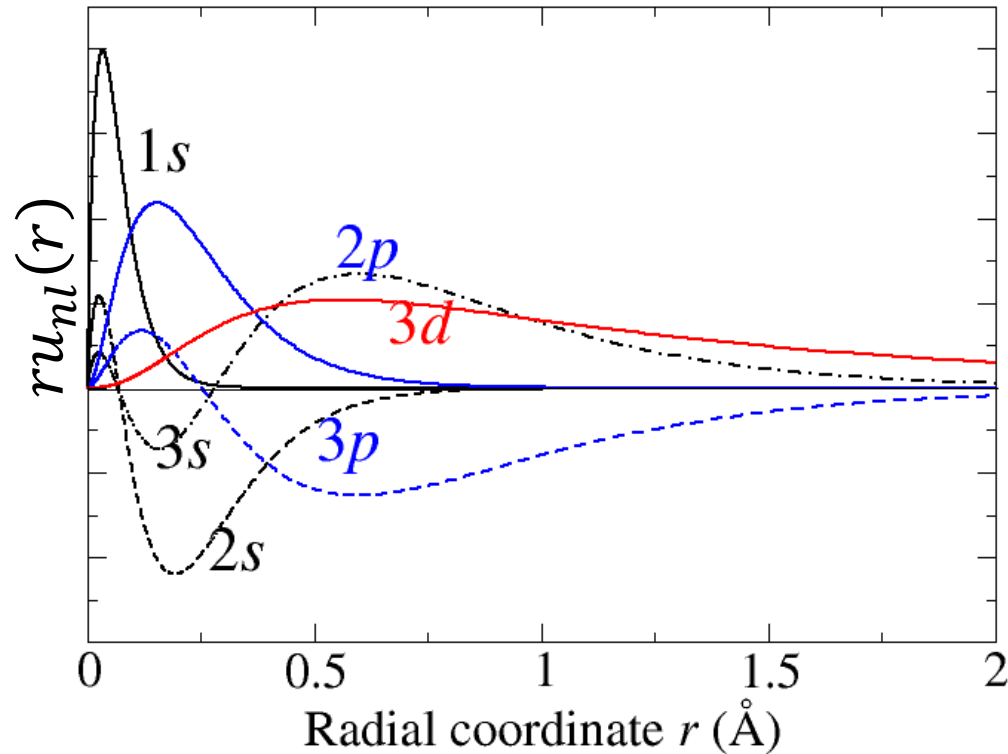
Consequence:

Prohibitively large amount of plane waves are needed to represent the wave function, not practical!

Consider a spherical atom ...

$$\left(-\frac{\nabla^2}{2m} - \frac{Z}{r} + V_{Hxc}(r) \right) \phi_{nlm}(\mathbf{r}) = \epsilon_{nl} \phi_{nlm}(\mathbf{r})$$

$$\phi_{nlm}(\mathbf{r}) = u_{nl}(r) Y_{lm}(\hat{\mathbf{r}})$$



Orthogonalized plane wave (OPW) method

Herring (1940)

$$\chi_{\mathbf{p}}(\mathbf{r}) = \left[\frac{1}{\sqrt{\Omega}} e^{i\mathbf{p}\cdot\mathbf{r}} - \sum_j \langle u_j | \mathbf{p} \rangle u_j(\mathbf{r}) \right]$$

$$\langle u_j | \mathbf{p} \rangle = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} u_j(\mathbf{r}) e^{i\mathbf{p}\cdot\mathbf{r}}, \quad \langle u_j | u_{j'} \rangle = \delta_{jj'}$$

$$\langle \chi_{\mathbf{p}} | \chi_{\mathbf{p}'} \rangle = \delta_{\mathbf{p},\mathbf{p}'} - \sum_j \langle \mathbf{p} | u_j \rangle \langle u_j | \mathbf{p}' \rangle$$

Using $\chi_{\mathbf{p}}(\mathbf{r})$ to expand the valence eigenfunctions of the atoms, the required number of basis functions can be significantly reduced. The local orbitals $u_j(\mathbf{r})$ are usually chosen as the core orbitals of the atom.

Applying the OPW method to atoms

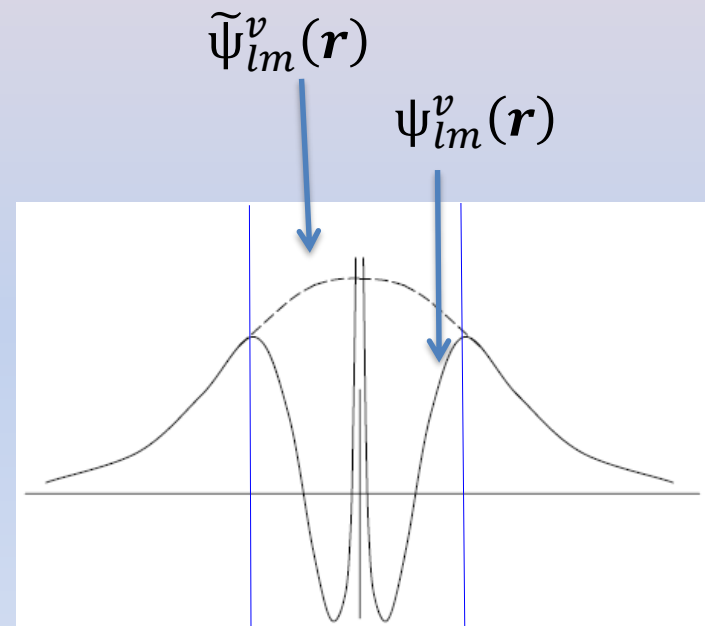
Expressing the valence states of the atom as:

$$\Psi_{lm}^v(\mathbf{r}) = \tilde{\Psi}_{lm}^v(\mathbf{r}) + \sum_j b_{lm,j} u_j(\mathbf{r})$$

$$\Psi_{lm}^v(\mathbf{r}) = \int d\mathbf{p} c_{lm}(\mathbf{p}) \chi_{\mathbf{p}}(\mathbf{r}) = \int d\mathbf{p} c_{lm}(\mathbf{p}) \left[\frac{1}{\sqrt{\Omega}} e^{i\mathbf{p}\cdot\mathbf{r}} - \sum_j \langle u_j | \mathbf{p} \rangle u_j(\mathbf{r}) \right]$$

$$\tilde{\Psi}_{lm}^v(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \int d\mathbf{p} c_{lm}(\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{r}}$$

$$b_{lm,j} = \int d\mathbf{p} c_{lm}(\mathbf{p}) \langle u_j | \mathbf{p} \rangle = \langle u_j | \tilde{\Psi}_{lm}^v(\mathbf{r}) \rangle$$



The true physical valence wave function is split into a smooth part plus a local oscillating part.

The PKA (Phillips & Kleinman, Antoncik) transform

Choose the core states as the projector function $u_j(\mathbf{r})$

$$u_j(\mathbf{r}) = \psi_{lm,j}^c(\mathbf{r}), \quad \hat{H}\psi_{lm,j}^c(\mathbf{r}) = \epsilon_{lj}^c \psi_{lm,j}^c(\mathbf{r})$$

Inserting $\psi_{lm}^v(\mathbf{r}) = \tilde{\Psi}_{lm}^v(\mathbf{r}) + \sum_j b_{lm,j} \psi_{lm,j}^c(\mathbf{r})$

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_{lm}^v(\mathbf{r}) = \epsilon_l^v \psi_{lm}^v(\mathbf{r})$$



$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) \right) \psi_{lm,j}^c(\mathbf{r}) = \epsilon_{l,j}^c \psi_{lm,j}^c(\mathbf{r})$$

$$\left(-\frac{\nabla^2}{2m} + V_{eff}(\mathbf{r}) + \hat{V}^R \right) \tilde{\Psi}_{lm}^v(\mathbf{r}) = \epsilon_l^v \tilde{\Psi}_{lm}^v(\mathbf{r})$$

$$\hat{V}^R \tilde{\Psi}_{lm}^v(\mathbf{r}) = \sum_j (\epsilon_{lj}^c - \epsilon_l^v) b_{lm,j} \psi_{lm,j}^c(\mathbf{r}), \quad b_{lm,j} = \langle \psi_{lm,j}^c | \tilde{\Psi}_{lm}^v \rangle$$

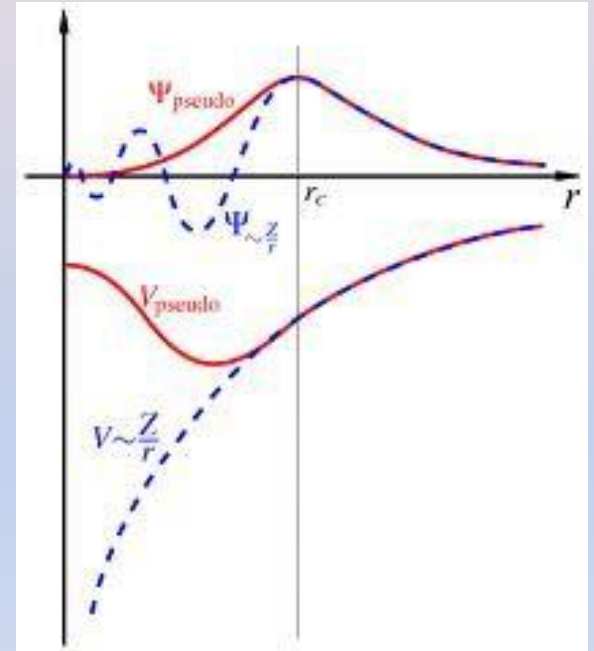
The concept of pseudopotential

$$\hat{V}^{\text{PKA}} = \hat{V}_{\text{eff}} + \hat{V}^R$$

The cancellation theorem:

\hat{V}^R is repulsive and cancels the $-Z/r$ part in \hat{V}_{eff} close to the nucleus. \hat{V}^{PKA} is much weaker than \hat{V}_{eff} .

\hat{V}^{PKA} is still not very smooth, and can be replaced by much simpler “model pseudopotentials”.



Pseudopotential is not unique!

Advantage of the pseudopotential approach

- In contrast to the PKA approach, the pseudopotential can be chosen at will, and does not depend on the pseudowavefunctions. Hence the pseudofunctions can be made orthonormal to each other.

$$\langle \tilde{\Psi}_i^{PS} | \tilde{\Psi}_j^{PS} \rangle = \delta_{ij}$$

- By doing ab initio calculations on atoms, and imposing conditions like “norm-conservation”, one can get highly accurate, transferable pseudopotentials that can be used in other chemical environments (molecules, solids, ...)

Requirement for “good” pseudopotentials

Hamann, Schluter, Chiang (1979)

- [1.] All-electron and pseudo valence eigenvalues agree for the chosen atomic reference configuration.
- [2.] All-electron and pseudo valence wavefunctions agree beyond a chosen core radius R_c .
- [3.] The logarithmic derivatives of the all-electron and pseudo wavefunctions agree at R_c .
- [4.] The integrated charge inside R_c for each wavefunctions agrees (**norm-conservation**).
- [5.] **The energy derivatives of the logarithmic derivatives** of the all-electron and pseudo wavefunctions agree at R_c .

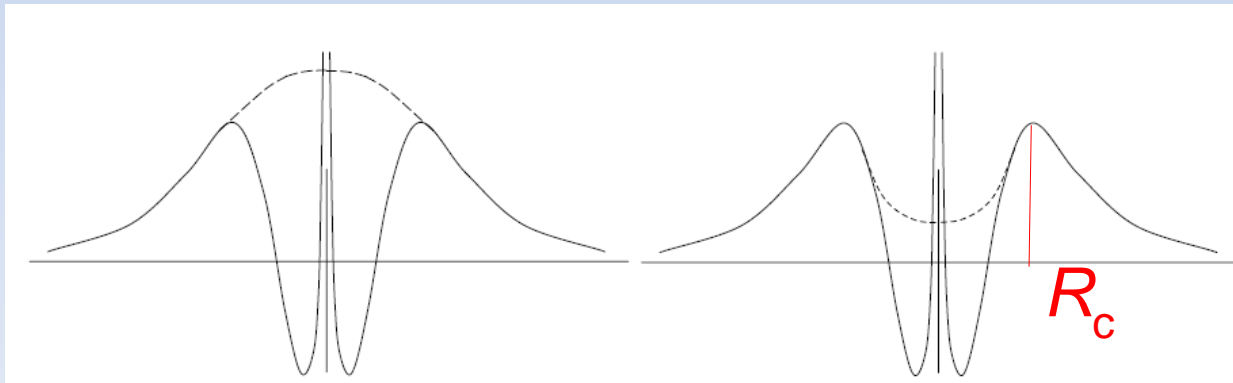
Requirement for “good” pseudopotentials

Logarithmic derivative:

$$D_l(\epsilon, r) = \frac{r\psi'_l(\epsilon, r)}{\psi_l(\epsilon, r)} = r \frac{d}{dr} \ln \psi_l(\epsilon, r)$$

Norm conservation: $Q_l = \int_0^{R_c} dr r^2 |\psi_l^{PS}(\mathbf{r})|^2 = \int_0^{R_c} dr r^2 |\psi_l^{AE}(\mathbf{r})|^2$

$\rightarrow \left[\frac{dD_l^{PS}(\epsilon, r)}{d\epsilon} \right]_{R_c} = \left[\frac{dD_l^{AE}(\epsilon, r)}{d\epsilon} \right]_{R_c}$ (Important for transferability !)



L -dependent norm-conserving pseudopotential

- Do all-electron atomic calculations at a given configuration, obtain the all-electron (AE) wave function $\psi_l^{AE}(r)$.
- Construct pseudopotential and wave function $\tilde{V}_l(r), \tilde{\psi}_l^{PS}(r)$ to reproduce ψ_l^{AE} beyond R_c .
- “Unscreening”: $V_l^{\text{Ion}}(r) = \tilde{V}_l(r) - V_{\text{Hxc}}^{\text{PS}}(r)$

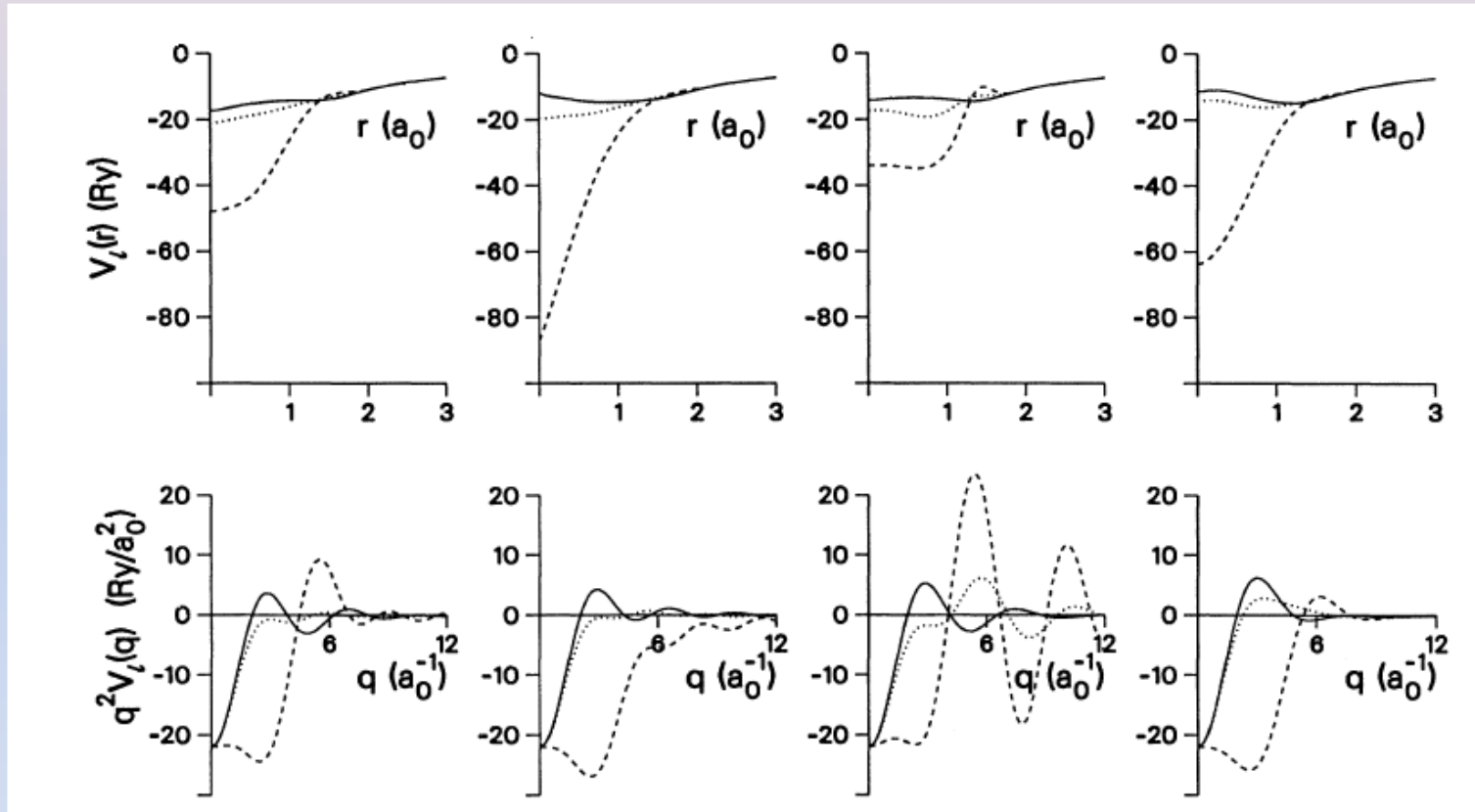


Pseudopotential due to valence electrons

- Semilocal form (SL): $V_l^{\text{Ion}}(r) = V_{\text{local}}(r) + \delta V_l(r)$

$$\hat{V}_{SL} = V_{\text{local}}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|$$

Different pseudopotentials exist ...



Troullier-Martins

Kerker

HSC

Vanderbilt

Separable pseudopotential operators

$$\hat{V}_{SL} = V_{local}(r) + \sum_{lm} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|$$

Computationally inefficient!

➔ Nonlocal (NL) separable potential

Reference
atomic pseudofunction

$$\hat{V}_{NL} = V_{local}(r) + \sum_{lm} \frac{|\psi_{lm}^{PS} \delta V_l\rangle \langle \delta V_l \psi_{lm}^{PS}|}{\langle \psi_{lm}^{PS} | \delta V_l | \psi_{lm}^{PS} \rangle}$$

$$\langle \psi_i | \delta \hat{V}_{NL} | \psi_j \rangle = \sum_{lm} \frac{\langle \psi_i | \psi_{lm}^{PS} \delta V_l \rangle \langle \delta V_l \psi_{lm}^{PS} | \psi_j \rangle}{\langle \psi_{lm}^{PS} | \delta V_l | \psi_{lm}^{PS} \rangle}$$

Kleinman & Bylander (1982)

L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)

The coupling between ψ_i, ψ_j are removed;

three-center integrals become two-center integrals!

Calculations with plane-wave basis sets

- Plane waves are the most natural basis for periodic systems

$$\tilde{\Psi}_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}=0}^{G_{cut}} c_{n,\mathbf{G}}(\mathbf{k}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

kinetic energy of plane waves:

$$-\frac{\hbar^2 \nabla^2}{2m} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = E^{kin} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$E_{cut}^{kin} = \hbar^2 \frac{|\mathbf{k} + \mathbf{G}_{cut}|^2}{2m}$$

The energy cutoff in plane-wave expansion determines the resolution that the wave function in the unit cell can be described.

The Hamiltonian matrix within plane basis

The Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}_{local}^{Ion} + \hat{V}_{NL}^{Ion} + \hat{V}_H + \hat{V}_{xc} = -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}_{local} + \hat{V}_{NL}^{Ion} + \hat{V}_H$$

The Hamiltonian matrix:

$$\langle \mathbf{k} + \mathbf{G} | \hat{H} | \mathbf{k} + \mathbf{G}' \rangle = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \delta_{\mathbf{G}, \mathbf{G}'} + V_{local}(\mathbf{G} - \mathbf{G}') + \frac{4\pi n(\mathbf{G} - \mathbf{G}')}{|\mathbf{G} - \mathbf{G}'|^2} + V_{\mathbf{G}, \mathbf{G}'}^{NL}(\mathbf{k})$$

$$V_{local}(\mathbf{G}) = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} V_{local}(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$n(\mathbf{G}) = \frac{1}{\sqrt{\Omega}} \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$V_{\mathbf{G}, \mathbf{G}'}^{NL}(\mathbf{k}) = \sum_{a, l, m} \langle \mathbf{k} + \mathbf{G} | p_{alm} \rangle V_{alm} \langle p_{alm} | \mathbf{k} + \mathbf{G}' \rangle$$

 Atomic projector functions

Solving the Hamiltonian

Even under the pseudopotential approximation, the number of plane waves are very many (a few hundreds per atom).

$$H_{G,G'}(\mathbf{k}) = \langle \mathbf{k} + \mathbf{G} | \hat{H} | \mathbf{k} + \mathbf{G}' \rangle$$

The Hamiltonian matrix is a big matrix, and a full diagonalization of the matrix is not practical. The standard way to deal with the problem is **iterative diagonalization**, from which one only gets the occupied and a small fraction of unoccupied energy spectra.

Standard algorithms for iterative diagonalization include:

- Davidson algorithm
- Conjugate gradient method

Computer codes

- Ab-initio

<http://www.abinit.org/>

- Quantum Espresso

<http://www.quantum-espresso.org/>